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Sub-Slab Air Permeability Testing and Air Sampling Using TO-17

Elements of Indoor Air/Sub-Slab Testing Protocol Being Developed by ORD

- Indoor and outdoor air sampling
- **Sub-slab vapor sampling**
- **Sub-slab air permeability testing**
- Screening using “ultra” sensitive PID or portable GC
- Radon/indoor air exchange rate testing

Why Sub-Slab Air Sampling?

“Conservativeness” of $\beta = 0.01$ in Q4?

$$\frac{d}{dZ} \left(\frac{dC_g}{dZ} \right) = 0 \quad \text{Subject to } C_g(0) = 0 \quad \text{and} \quad C_g(Z_{(source)}) = C_{g(source)}$$

$$\text{Results in } C_{g(sub-slab)} = \frac{Z_{(sub-slab)}}{Z_{(source)}} C_{g(source)}$$

$$\text{let } \beta = \frac{C_{g(indoor)}}{C_{g(sub-slab)}} \quad \text{and} \quad \alpha = \frac{C_{g(indoor)}}{C_{g(source)}}$$

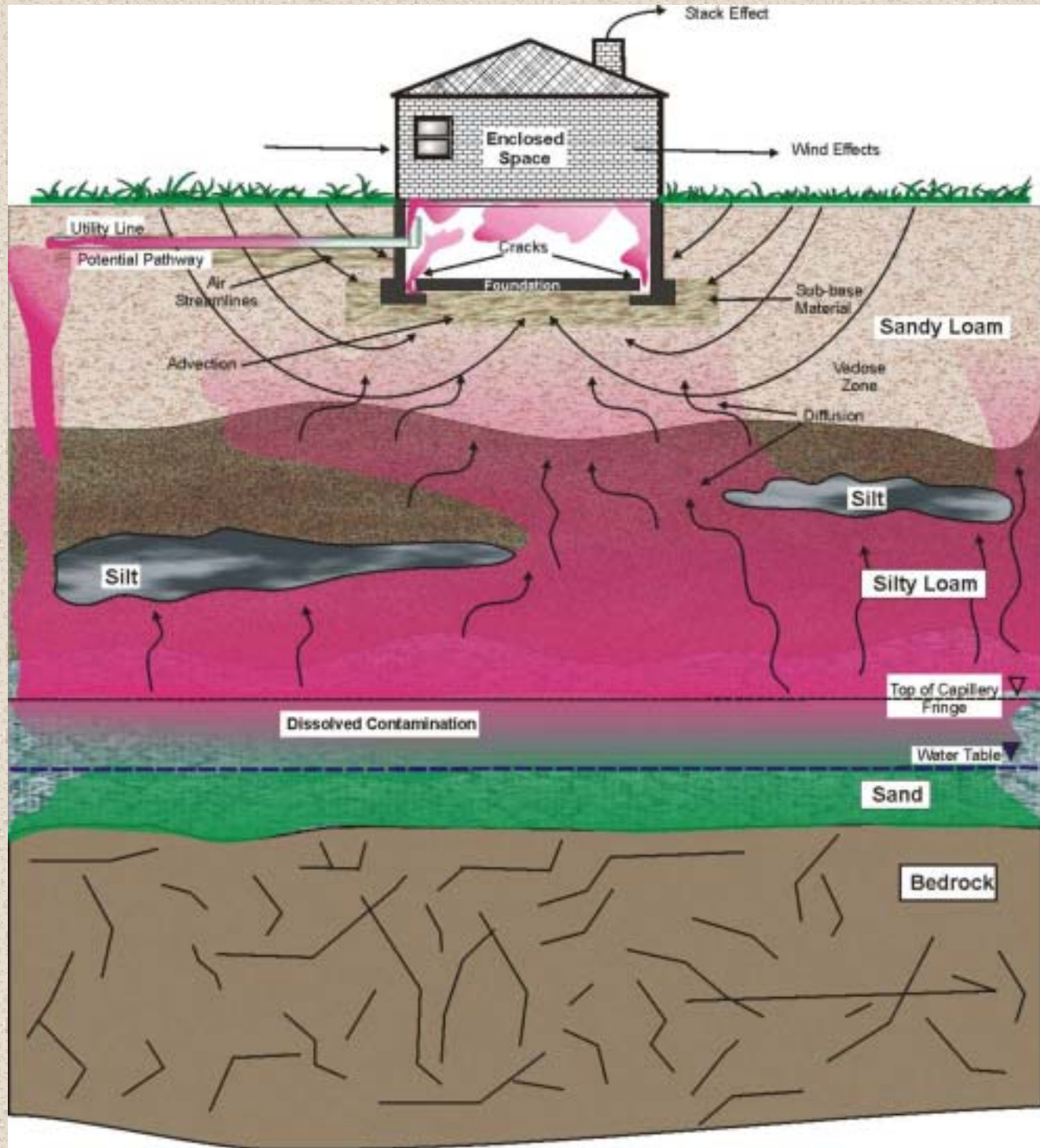
$$\text{then } \alpha = \frac{Z_{(sub-slab)}}{Z_{(source)}} \beta$$

And the following condition must be met which can only be guaranteed when $\beta < 0.01$

$$\frac{Z_{(sub-slab)}}{Z_{(source)}} \beta \leq 0.01$$

Example Calculation

If $\beta = 0.1$, and $Z_{(\text{sub-slab})} = 5$ feet, then $Z_{(\text{source})}$ must be $>$ than 50 feet for $\alpha < 0.01$. Use of $\alpha = 0.01$ at < 50 feet would hypothetically result in exposure.

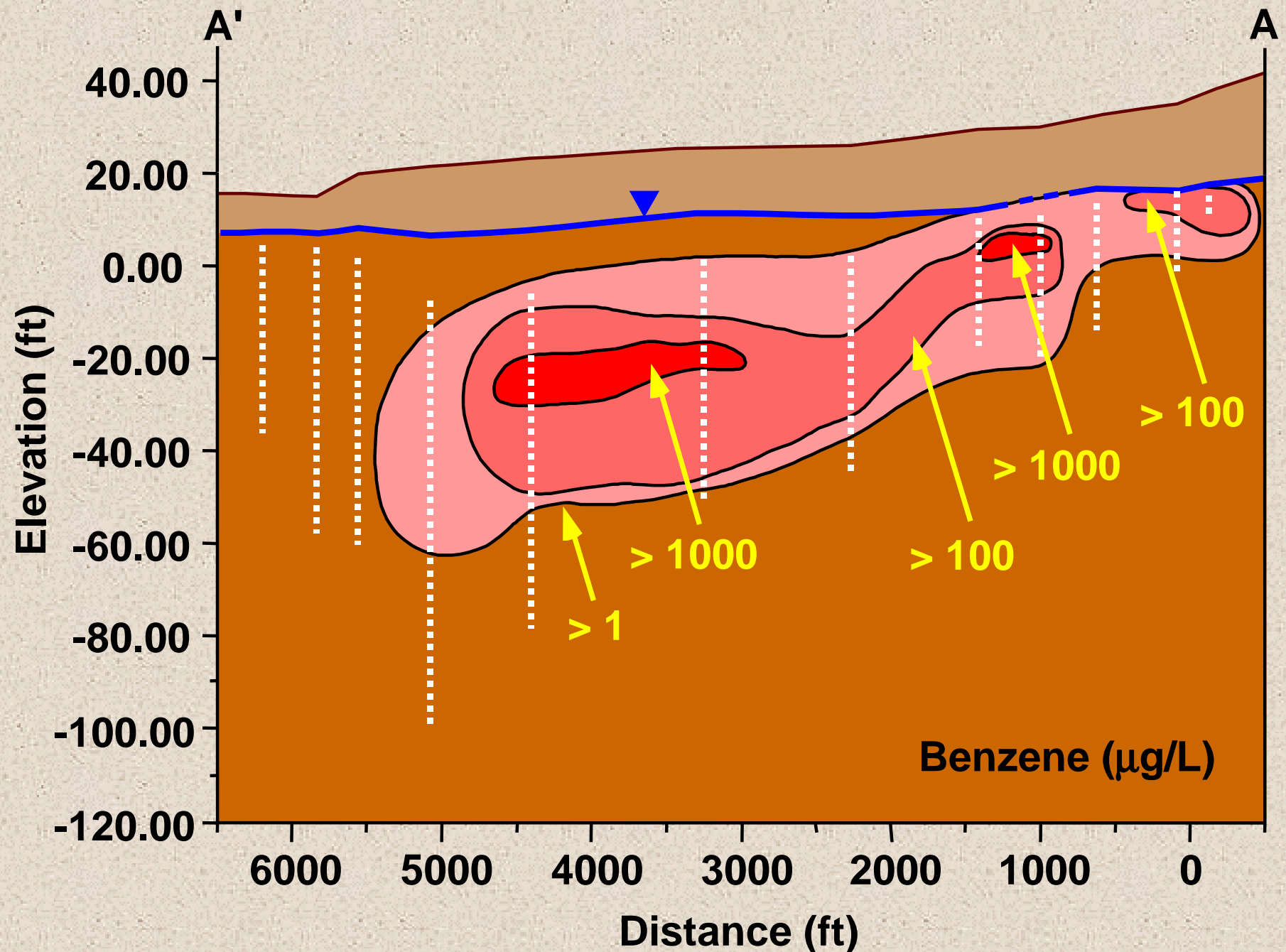


Uncertainty in ground-water plume delineation

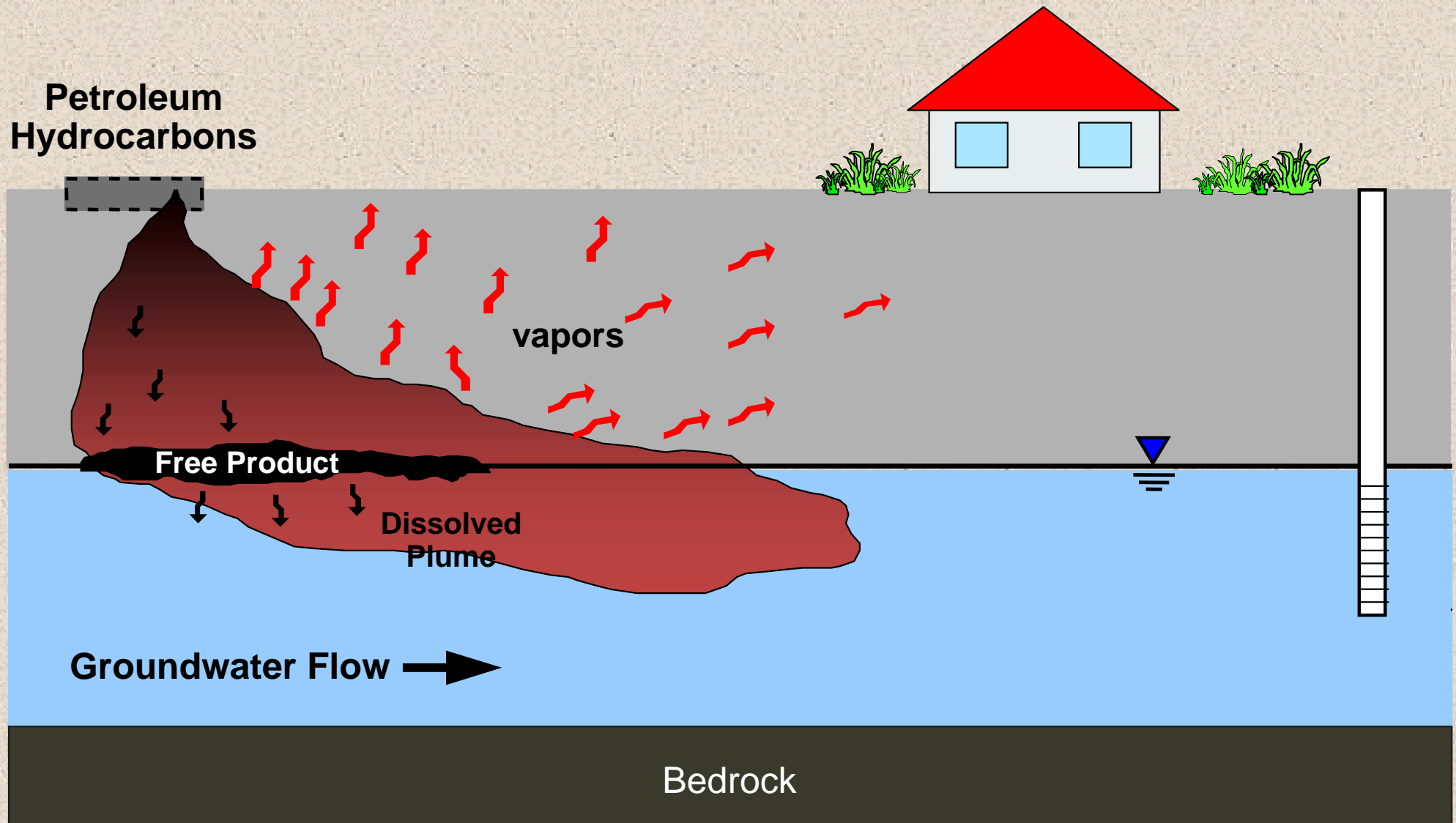
For a ground-water source term, use of $\alpha = 0.01$ and the J&E model will be dependent in most cases on interpolated and extrapolated concentrations from a few off-site monitoring wells. How well are the areal and vertical extent of plumes delineated at Superfund, RCRA, and UST sites?

A recent review* of 20 fund-lead pump and treat systems at Superfund sites revealed that ground-water plumes were adequately delineated at only 8 of these sites (40%).

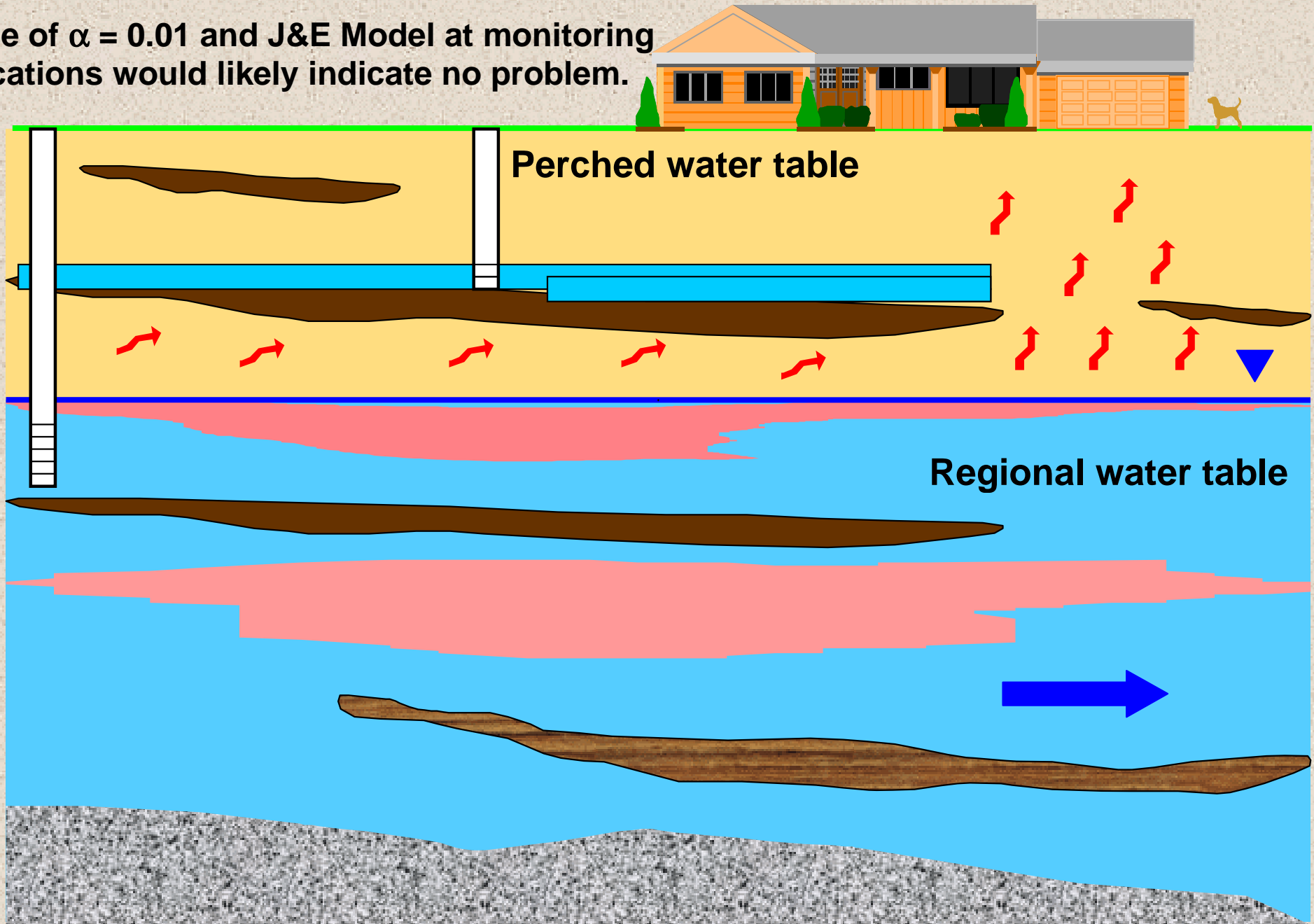
Example of well-defined vertical transect using Discrete Multi-Level Sampling Devices. Is this practical at most sites? Expense?



Lateral vapor transport - Use of $\alpha = 0.01$ and J&E Model at monitoring location would likely indicate no problem.

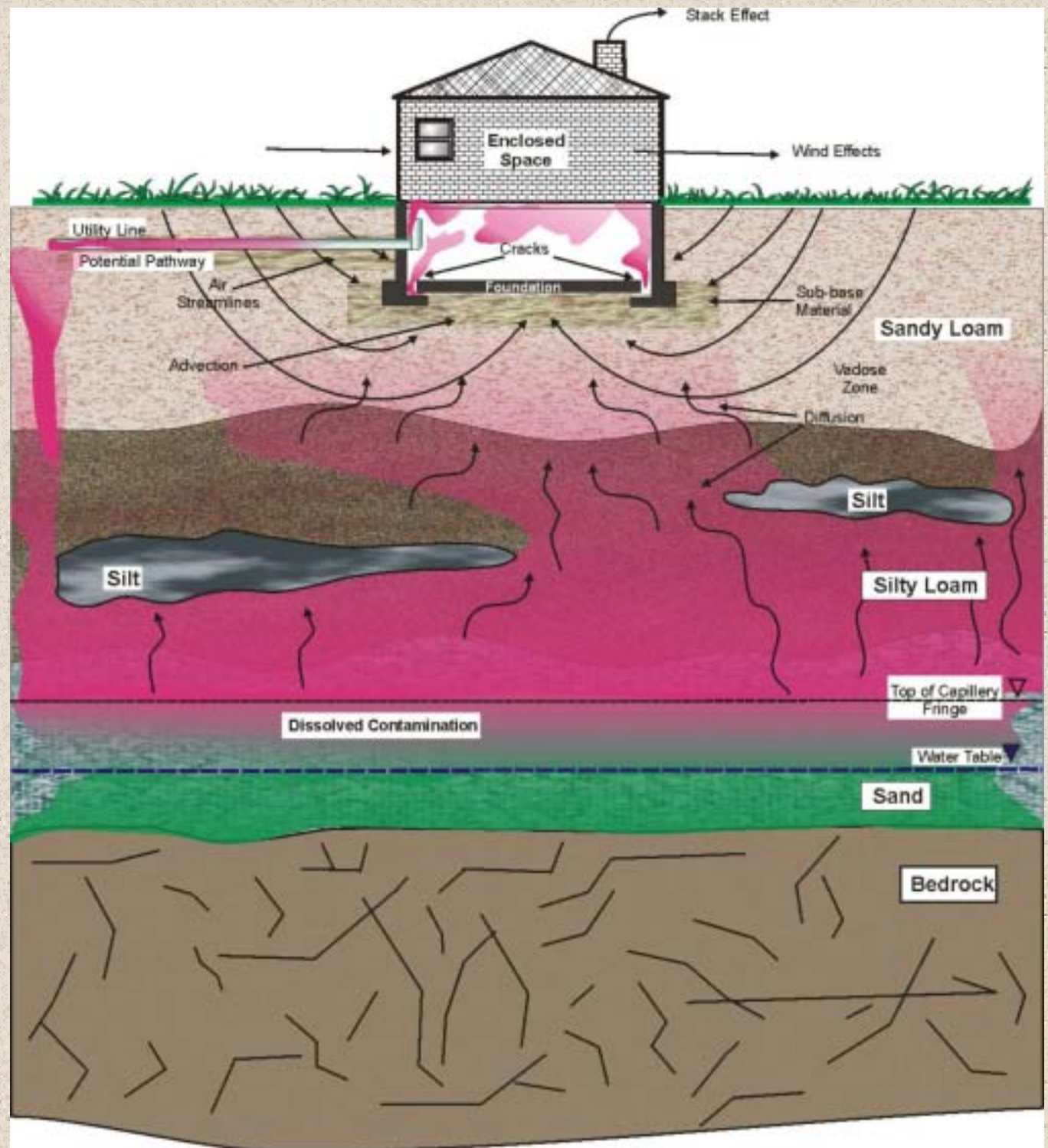


Use of $\alpha = 0.01$ and J&E Model at monitoring locations would likely indicate no problem.



Layered soils

–Use of $\alpha = 0.01$
and J&E model
would be allowed
in this situation.



**Use of J&E model precluded in this situation.
Is the use of $\alpha = 0.01$ valid here?**



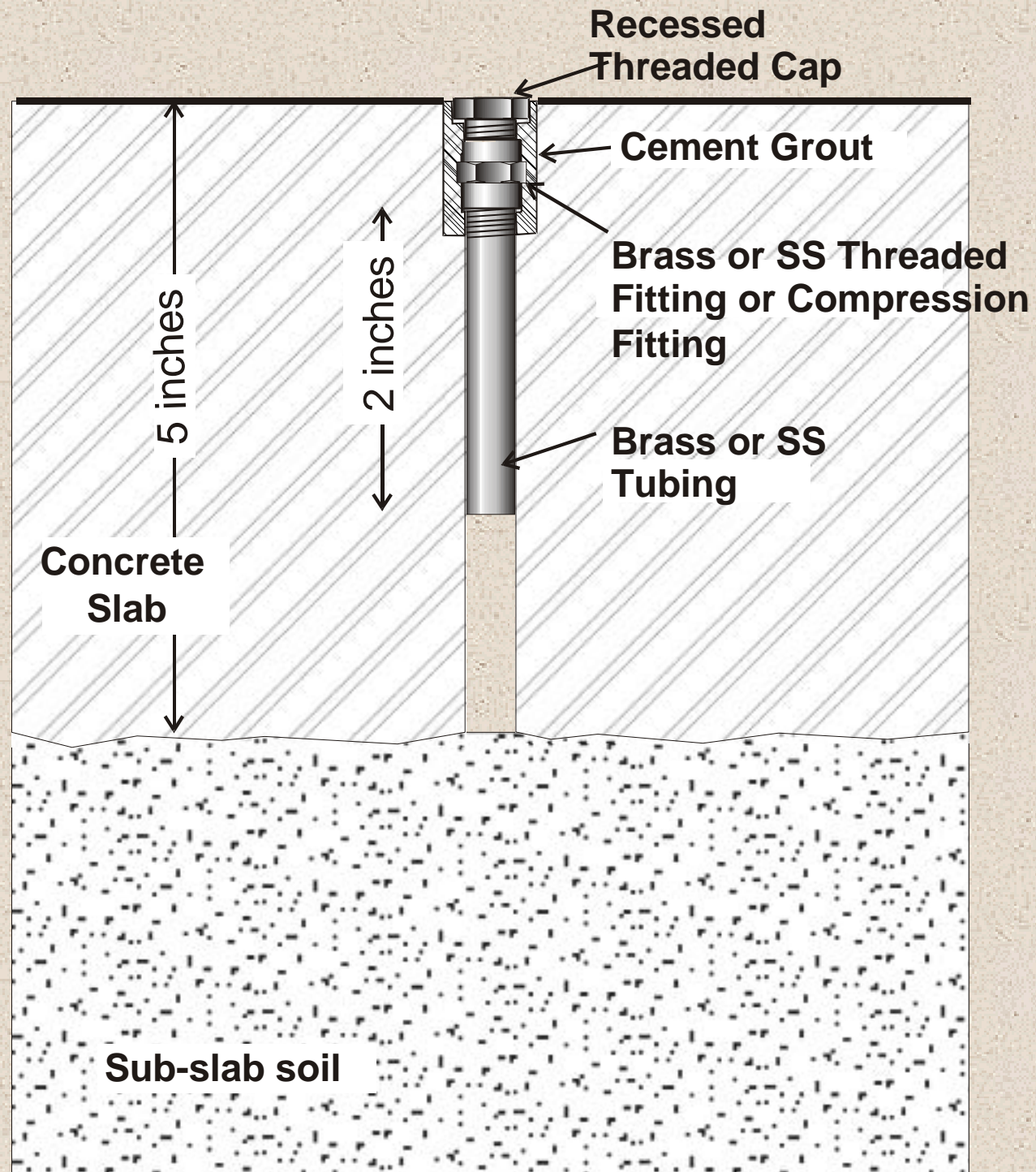
Use of Johnson & Ettinger Model in Q5?

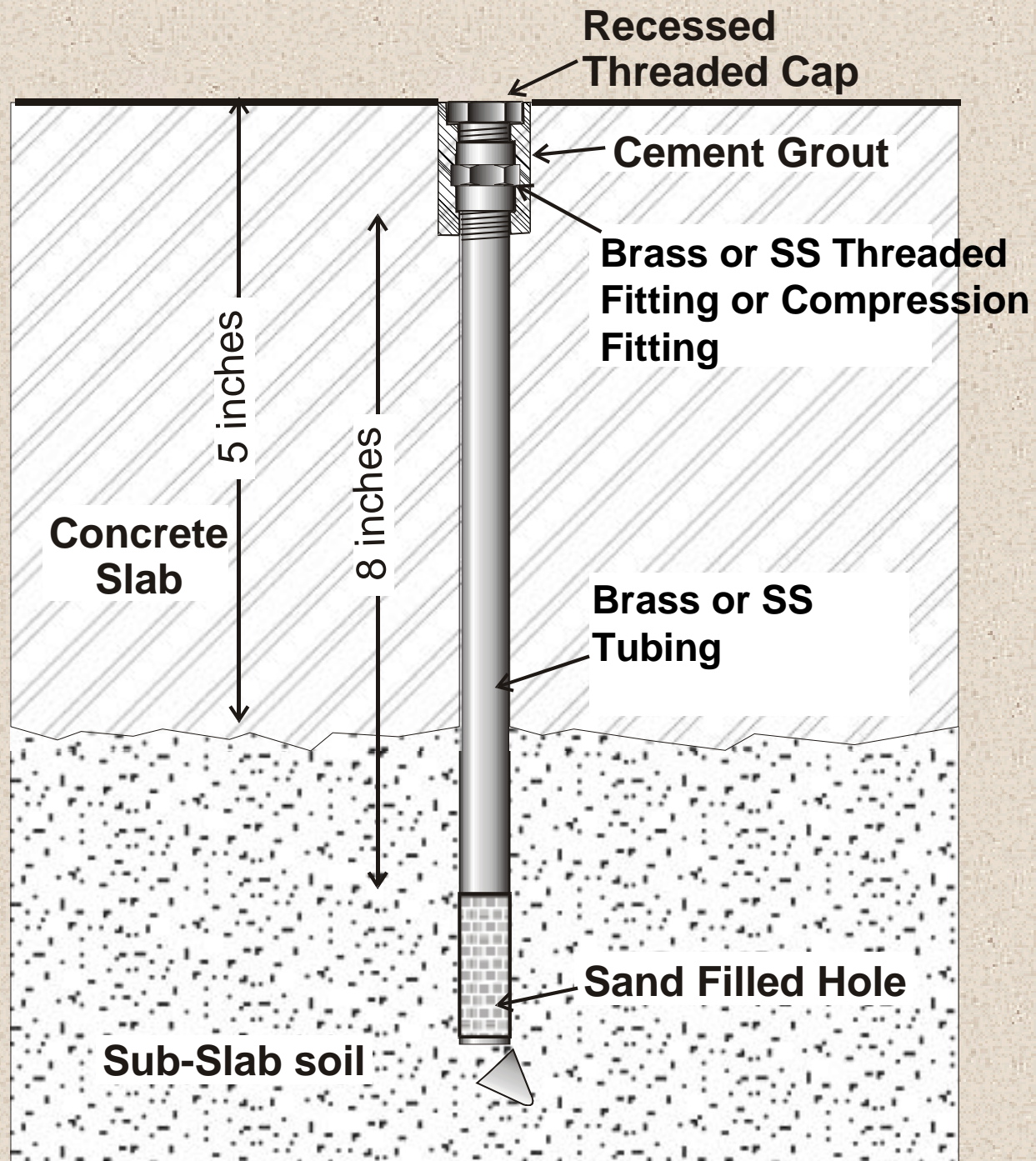
- Direct use in screening ignores potential for preferential migration through utility lines
- Significant uncertainty in concentration and depth of “source”
- Will be used in but cannot simulate first-order transport process in deep or non-homogeneous systems (transient transport, layered systems or systems with discontinuous lenses where 2-D or 3-D transport would dominate, preferential movement through vertical fractures in structured soils)
- Danger of “creative” model application or use of model in lieu of data to ensure incomplete pathway
- Uncertainty in vadose zone in “constrained” model parameters to ensure “**conservative**” (undefined when model does not simulate first-order processes) application – nonlinear propagation of errors

Sub-Slab Testing Allows

- Definitive (relative to modeling and subsurface media sampling) assessment of vapor intrusion (not limited by inadequate site-characterization and modeling)
- Collection of sub-slab depressurization design information (air permeability and air flow continuity under slab)
- Immediate mitigation if required (through 1" diameter hole in center of slab used during air permeability testing and portable pump)

Probe Installation





QA: Methanol Extraction of Brass Fittings and Cement Grout for Background VOCs



Drilling Small-Diameter Hole Through A Slab



Over-drill bit to Create 1" Long Recessed Hole



Completed Hole



Grouted Hole with Vapor Probe



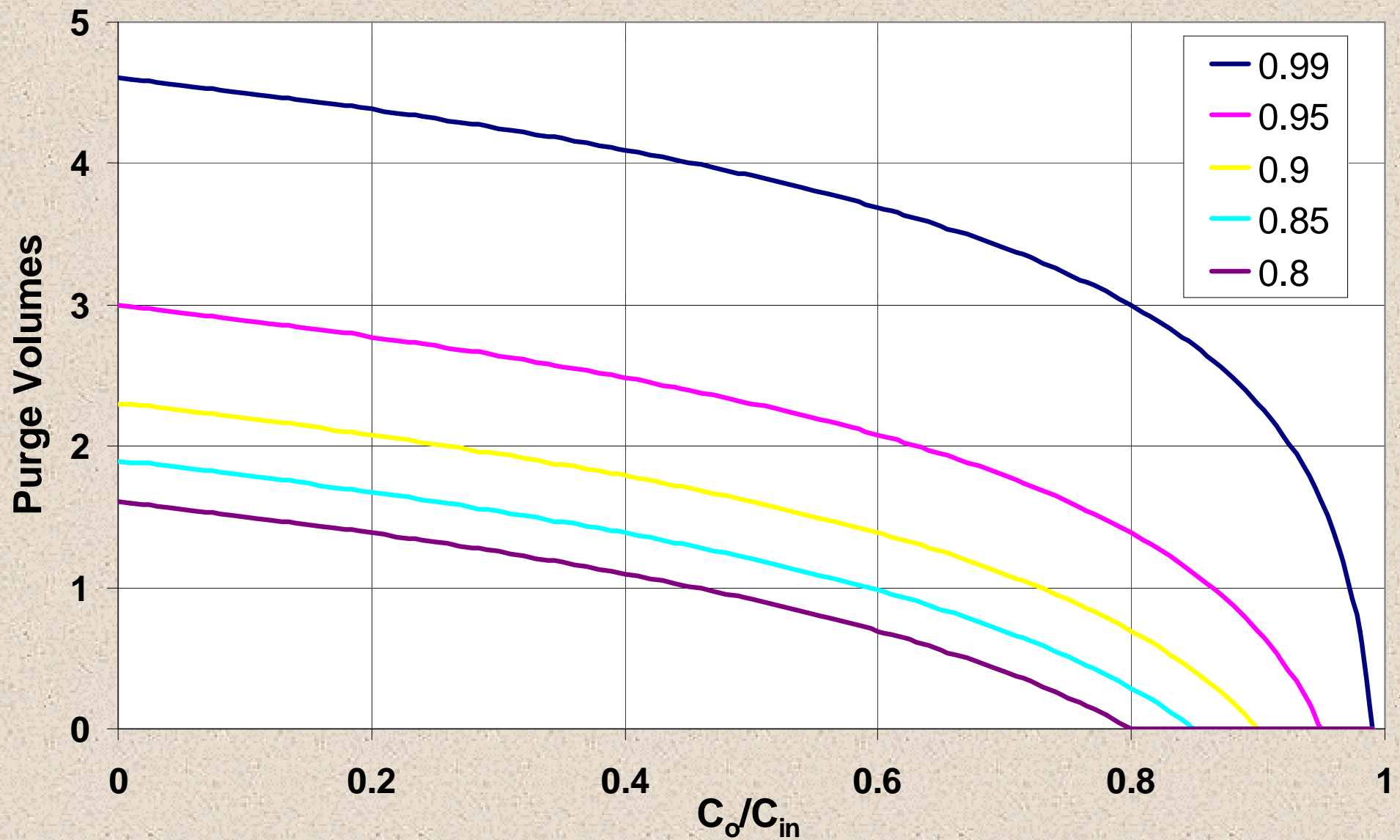
Sub-Slab Air Sampling

QA: Calculation of Purge Volume

$$\frac{dm}{dt} = Q \left(C_{in} - \frac{m(t)}{V} \right) \quad C(0) = C_0$$

$$\text{purge volume} = \frac{tQ}{V} = - \left[\ln \left| \frac{1 - C(t) / C_{in}}{1 - C_0 / C_{in}} \right| \right]$$

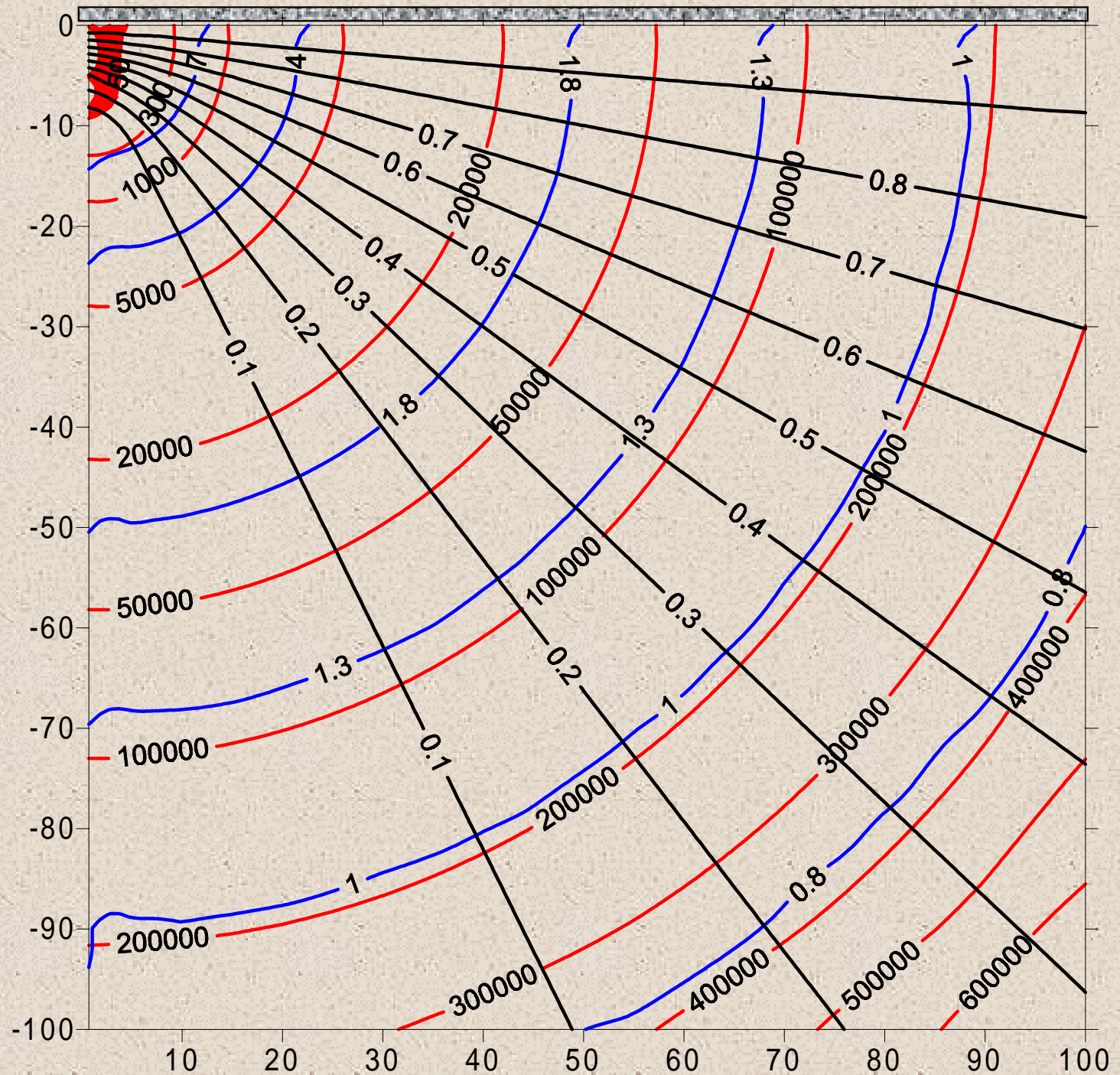
QA: Purge Volume (tQ/V) as a Function of $C(t)/C_{in}$



QA: Sample area

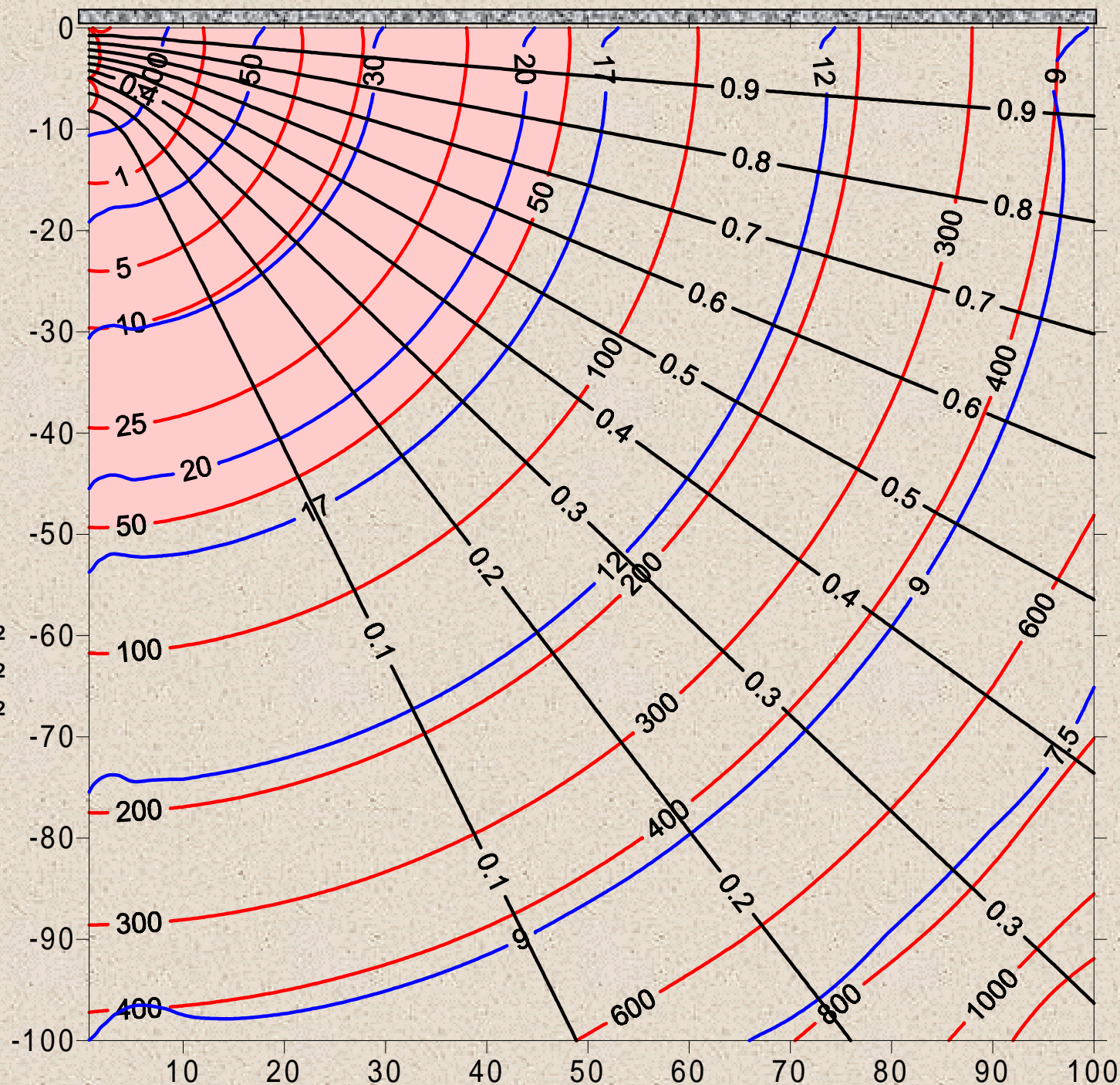
Simulated pressure differential (Pa), streamlines, and travel time (min) below a slab during air sampling at 100 cc/min

$L_{\text{slab}} = 13 \text{ cm}$
 $L_{\text{water-table}} = 1000 \text{ cm}$
 $K_{\text{slab}} = 1.0 \times 10^{-10} \text{ cm}^2$
 $K_{\text{sub-slab}} = 5.0 \times 10^{-08} \text{ cm}^2$
 $K_{\text{soil}} = 5.0 \times 10^{-08} \text{ cm}^2$
 $R_w = 0.7 \text{ cm}$
 $\alpha_g = 0.2$



**Simulated pressure
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**Compendium of Methods
for Determination of Toxic
Organic Compounds
in Ambient Air**

Second Edition

Compendium Method TO-17

**Determination of Volatile Organic
Compounds in Ambient Air Using Active
Sampling Onto Sorbent Tubes**

**Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268**

January 1999

Advantages of Compendium Method TO-17

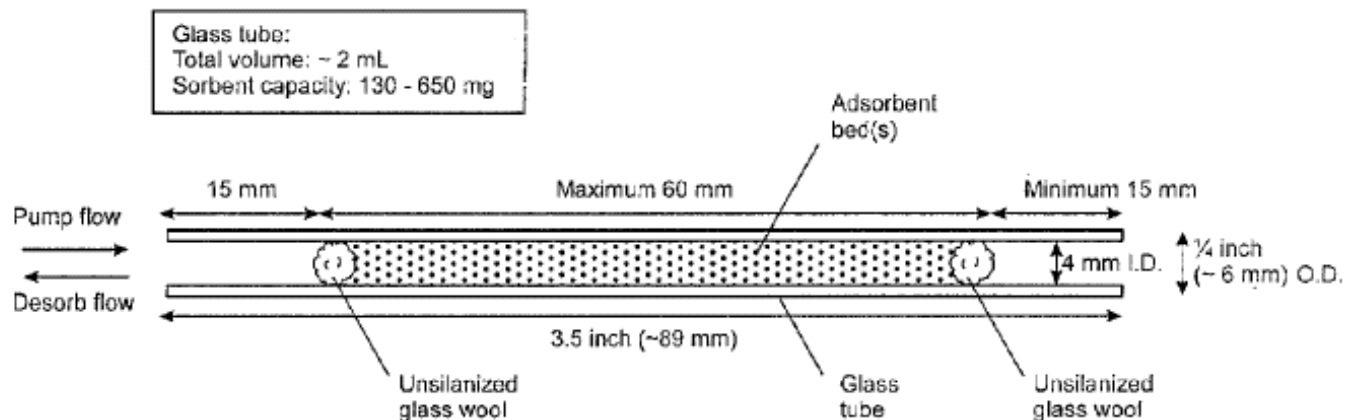
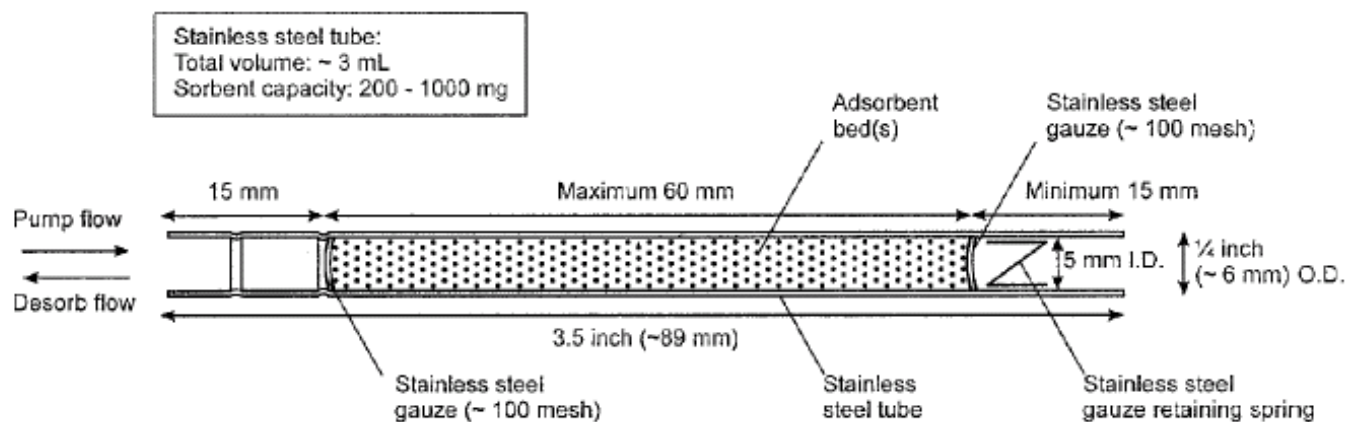
- EPA approved method for both sampling and analysis
- Rigorous QA/QC requirements (exceeds ASTM methods)
- Detection limits for all VOCs in ambient air required at 0.5 to 25 ppbv level (pptv for highly halogenated compounds with ECD and compounds with high safe sampling volumes)
- Commercial availability of thermal desorption units and large selection of sorbents
- Small size and weight of sorbent packing and attendant equipment
- Possibility of moisture management by dry purging and sample splitting prior to injection into GC
- Large amount of published literature
- Active area of development

Sorbent Tube Design and Conditioning

Tube Conditioning

- 350C for 2 hours with >50 ml/min He
- wrap in uncoated Al
- Place in container w/activated carbon
- store at 4 C

Artifacts must be reduced to < 10% of individual analyte mass



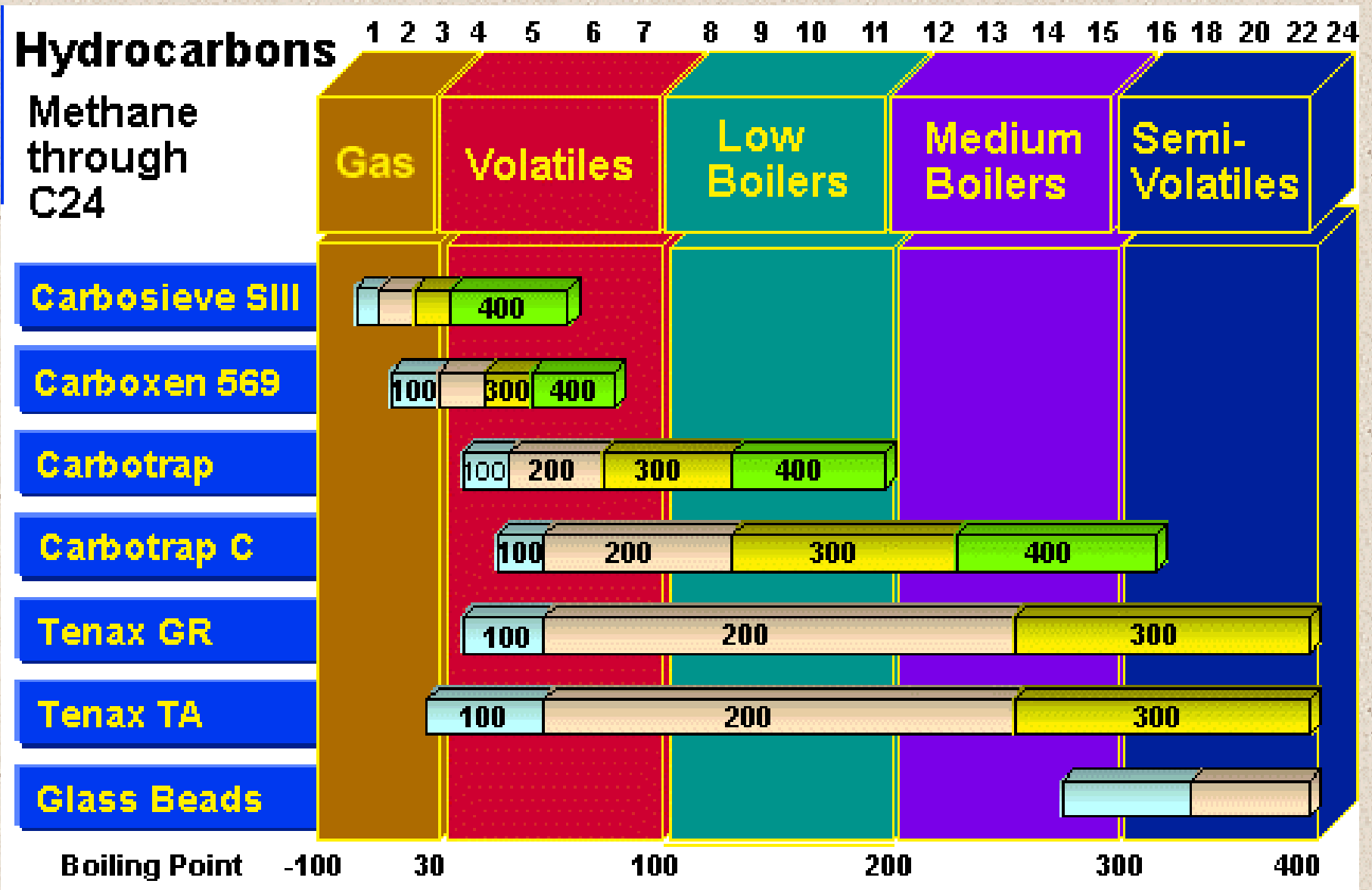
Limited Summary of Available Sorbents

Sorbent	Analyte Volatility	Surface Area (m ² /g)	Example Analytes
CarbotrapC® CarbopackC ® Anasorb®GCB2	n-C ₈ to n-C ₂₀	12	Alkyl benzenes and aliphatics
Tenax ®TA	n-C ₈ to n-C ₂₀ bp 100°C to 400°C	35	Aromatics except benzene, nonpolar compounds (bp>100°C) and less volatile polar compounds (bp>150°C)
Tenax GR	n-C ₇ to n-C ₃₀ bp 100°C to 450°C	35	Alkyl benzenes, vapor phase PAHs and PCBs, and as above for Tenax ®TA
Carbotrap® CarbopackB ® Anasorb®GCB1	n-C5 to n-C14	100	All n-C5 to n-C14 nonpolar compounds, perfluorocarbon tracers, ketones, alcohols, and aldehydes (bp>75°C)
Chromosorb ® 102	bp 50°C to 200°C	350	Wide range of VOCs including oxygenated compounds and haloforms less volatile than methylene chloride
Chromosorb106	bp 50°C to 200°C	750	Wide range of VOCs and volatile oxygenated compounds
Porapak Q	n-C5 to n-C12 bp 50°C to 200°C	550	Wide range of VOCs and volatile oxygenated compounds
Porapak N	n-C5 to n-C8 bp 50°C to 150°C	300	Volatile nitriles, alcohols, and ketones
Spherocarb*	N-C3 to n-C8 bp -30°C to 150°C	1200	Good for very volatile compounds (e.g., vinyl chloride) and polar compounds
Carbosieve SIII* ® Caroxen 1000* ® Anasorb CMS*	bp -60°C to 80°C	800	Good for ultra volatile compounds, haloforms, and freons

* Not hydrophobic

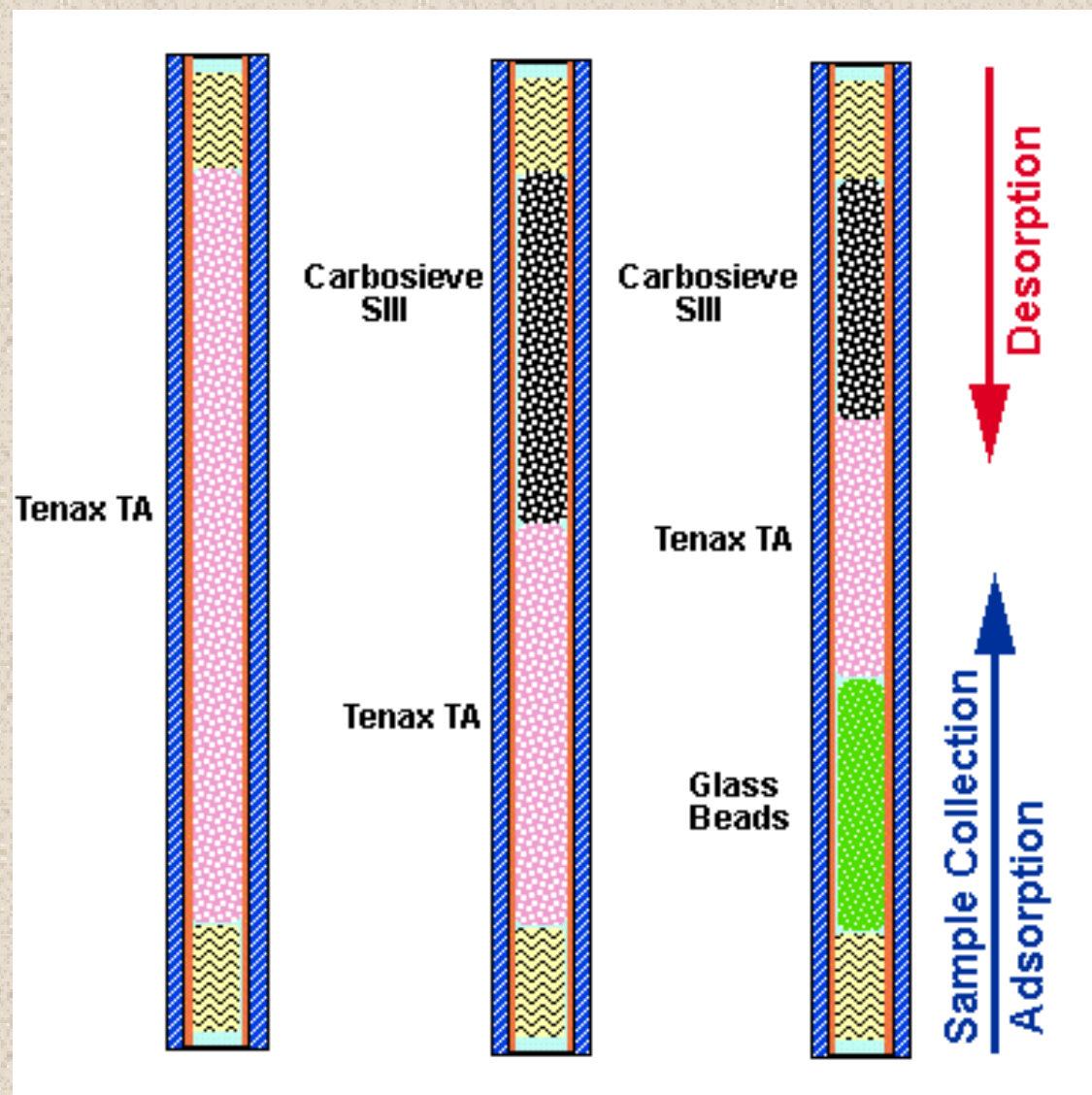
Source: TO-17

Sorbent Selection



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Mixed Resin Beds



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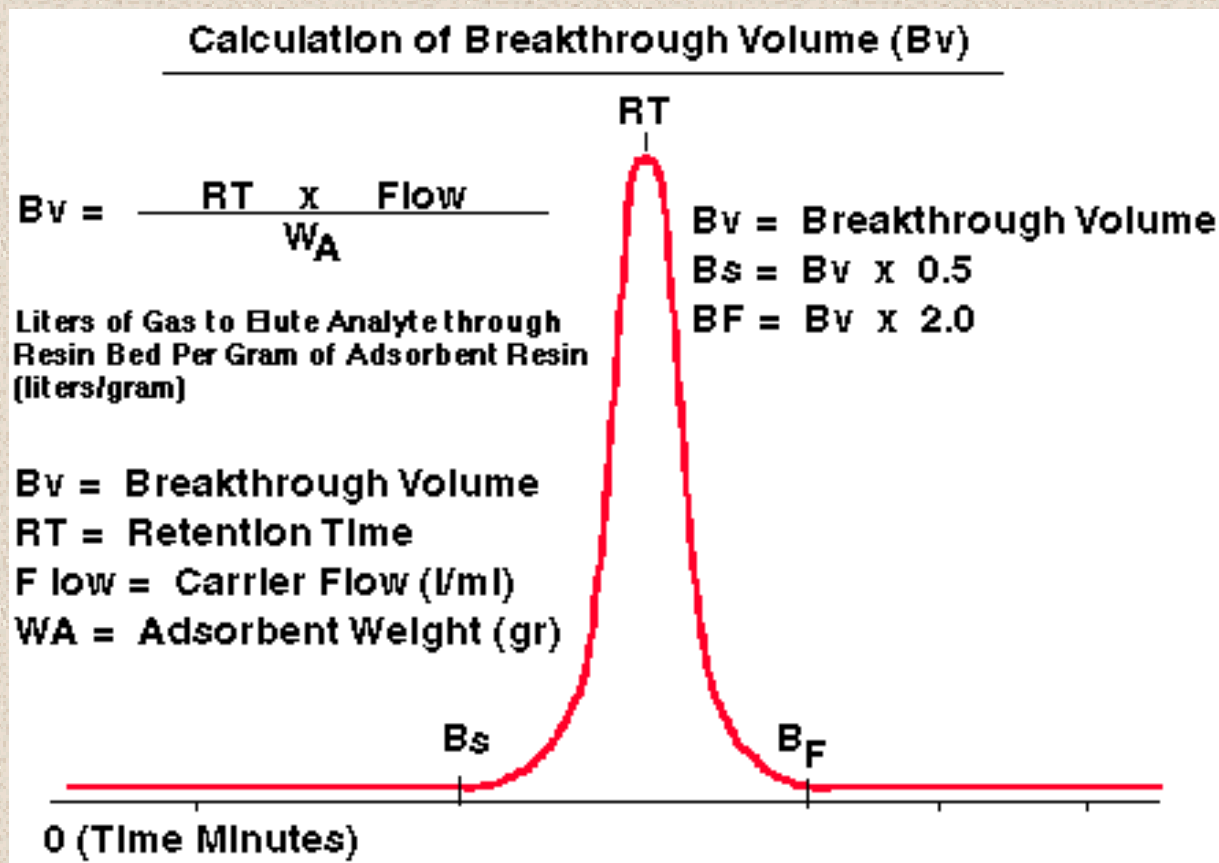
Breakthrough Volume

EPA Definition of Breakthrough Volume

“volume of air containing a constant concentration of analyte which may be passed through a sorbent tube before a detectable level (typically 5%) of the analyte elutes from the nonsampling end.”

EPA defines a safe sampling volume = 2/3 breakthrough volume

Reduce safe sampling volumes by a factor of 10 at > 90% RH for non-hydrophobic sorbents



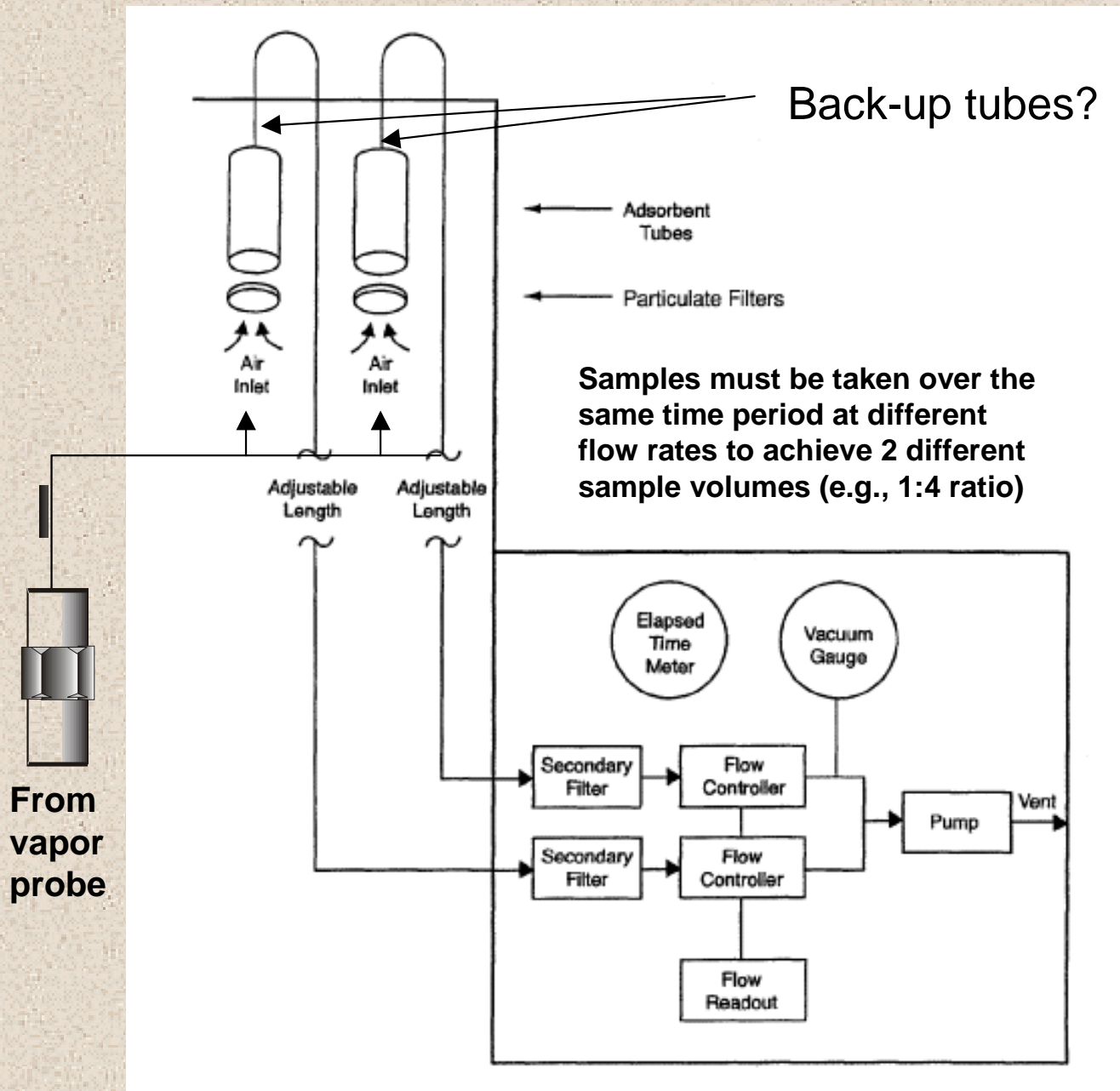
Temperature of sorbent tube must be the same or higher than sampled air!

Breakthrough Volumes on Carboxen 569

Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340
Monochlorodifluoromethane	2.00	1.00	0.500	0.230	0.130	0.060	0.031	0.020	0.013	0.009	0.007	0.005	0.004	0.003	0.002	0.001		
Trichlorofluoromethane	5.00	3.10	1.90	1.20	0.730	0.460	0.290	0.180	0.105	0.067	0.040	0.025	0.016	0.010	0.007	0.004	0.003	0.002
Monochloromethane	12.0	6.00	3.00	1.50	0.800	0.400	0.198	0.102	0.062	0.040	0.025	0.018	0.014	0.011	0.008	0.006	0.003	0.002
Dichlorodifluoromethane	18.0	6.00	2.30	1.00	0.450	0.177	0.072	0.039	0.021	0.013	0.008	0.005	0.003	0.002	0.002	0.001		
Vinylchloride	21.0	12.0	8.00	4.60	2.80	1.70	1.00	0.600	0.370	0.235	0.137	0.081	0.053	0.040	0.028	0.020	0.016	0.011
Methylenechloride	70.0	38.0	20.0	10.5	5.70	3.00	1.50	0.800	0.444	0.230	0.114	0.070	0.042	0.030	0.022	0.015	0.009	0.004
1,1-Dichloroethylene	72.0	42.0	23.0	13.0	7.80	4.30	2.40	1.40	0.800	0.430	0.260	0.140	0.084	0.051	0.031	0.023	0.010	0.005
1,1-Dichloroethane	700	300	130	52.0	22.0	9.30	4.00	1.70	0.698	0.288	0.127	0.065	0.044	0.028	0.021	0.015	0.010	0.007
Chloroform	570	240	120	52.0	23.0	10.5	5.00	2.10	1.00	0.407	0.178	0.087	0.050	0.036	0.026	0.017	0.013	0.009
Tetrachloromethane	570	240	120	52.0	23.0	10.5	5.00	2.10	1.00	0.420	0.201	0.094	0.050	0.036	0.021	0.014	0.01	0.004
1,1,1-Trichloroethane	570	240	120	52.0	23.0	10.5	5.00	2.10	1.00	0.384	0.185	0.081	0.046	0.031	0.019	0.014	0.009	0.006
1,2-Dichloropropane	260	150	80	45.0	26.0	14.0	8.00	4.20	2.30	1.30	0.700	0.400	0.211	0.121	0.067	0.039	0.020	0.011
1,2-Dichloroethane	300	160	85	45.0	24.0	13.0	7.00	3.70	2.00	1.00	0.550	0.288	0.147	0.086	0.057	0.037	0.030	0.023
Bromodichloromethane	700	320	130	70.0	34.0	18.0	9.00	4.20	2.00	1.00	0.515	0.246	0.110	0.067	0.038	0.020	0.010	0.006
Trichloroethylene	600	330	200	105	60.0	33.0	20.0	10.5	6.00	3.30	2.00	1.05	0.6	0.332	0.195	0.110	0.070	0.004
1,1,2-Trichloroethane	500	270	150	80.0	43.0	23.0	13.0	7.00	4.00	2.10	1.10	0.600	0.330	0.183	0.099	0.057	0.030	0.020
Dibromochloromethane	1,800	900	400	200	90.0	42.0	20.0	10.0	4.40	2.10	1.00	0.48	0.22	0.106	0.060	0.033	0.018	0.010
Bromoform	10,000	5000	2000	950	400	170	80.0	33.0	15.0	6.60	3.00	1.20	0.55	0.236	0.109	0.045	0.020	0.010
1,2-Dichloroethylene	10,500	5,500	2300	1050	500	230	105	50.0	21.0	10.0	4.30	2.00	0.9	0.397	0.183	0.103	0.060	0.040
1,3-dichloropropene	20,000	8,000	3300	1400	600	270	110	50.0	20.0	9.60	3.90	1.70	0.7	0.288	0.123	0.050	0.025	0.011
1,1,2,2-Tetrachloroethane	20,000	10000	4500	2000	1000	450	205	100	48.0	21.0	10.0	4.80	2.10	1.00	0.531	0.200	0.100	0.057
Chlorobenzene	40,000	20000	11000	6000	3100	1800	900	500	280	130	80.0	40.0	21.0	11.0	6.00	3.10	1.80	0.983

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TO-17 QA Requirements - Distributive Air Volume Sampling

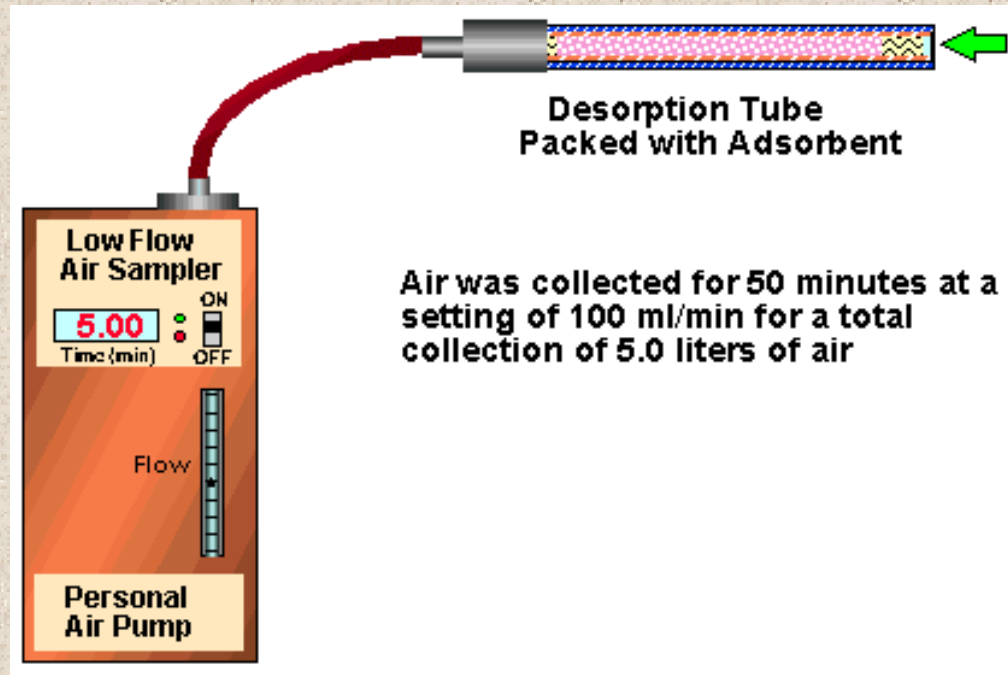


$$\left\{ \frac{|X1 - X2|}{\bar{X}} 100 \right\} \leq 25\%$$

Distributive air volume sampling provides “inherently defensible data to counter questions of sample integrity, operator performance, equipment malfunction during sampling, and any other characteristics of sample collection that is not linear with sampling volume.”

Sampling rate (r)
 10 ml/min > r > 200 ml/min

TO-17 QA Requirements: Sampling Pumps



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Sampling pumps must:

- be able to achieve targeted sample flow rates
- be certified traceable to NIST standards
- be calibrated before and after each sampling event
- achieve constant flow (within 10% during sampling)

Back Pressure

Tenax TA Back Pressures for 3.0 mm I.D. Desorption Tubes

mg Tenax TA	25 ml/min	50 ml/min	75 ml/min	100 ml/min	125 ml/min
50	7.5	14.5	22	29	36
100	11.5	23	33.5		
150	36.5				

Tenax TA Back Pressures for 4.0 mm I.D. Desorption Tubes

mg Tenax TA	25 ml/min	50 ml/min	75 ml/min	100 ml/min	125 ml/min	150 ml/min	175 ml/min	200 ml/min
50	2	4	6.5	8	10.5	12	14	16.5
100	3.5	7	10.5	13.5	17	20	23.5	27.5
150	5	10	15	19	24	28.5	31.5	39
200	7.5	14.5	21.5	29	35.5			
250	10	20	30.5					

Back Pressure expressed in inches of water

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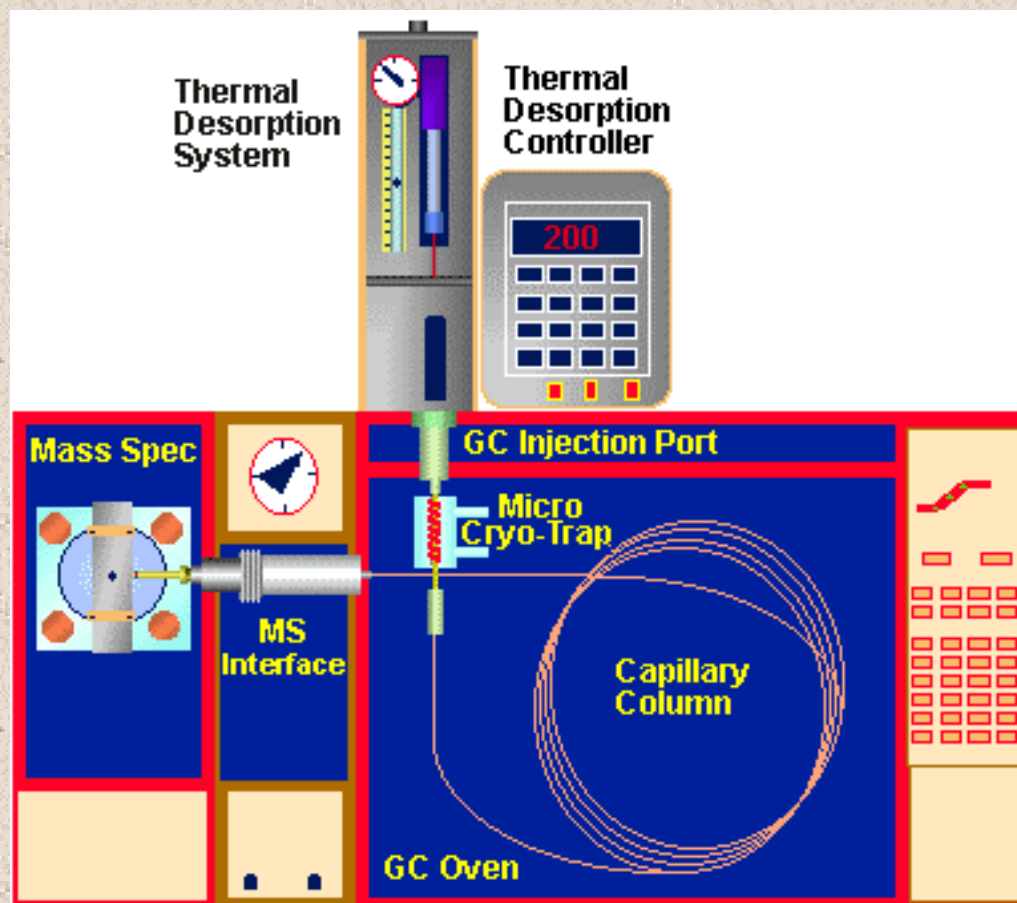
Example Thermal Desorption System

Key steps in sample analysis

- Dry purge to remove water
- Thermal desorption of primary tube
- Refocusing on secondary trap
- Rapid desorption into GC
- Separation by capillary GC
- Measurement by MS, PID, FID, ECD

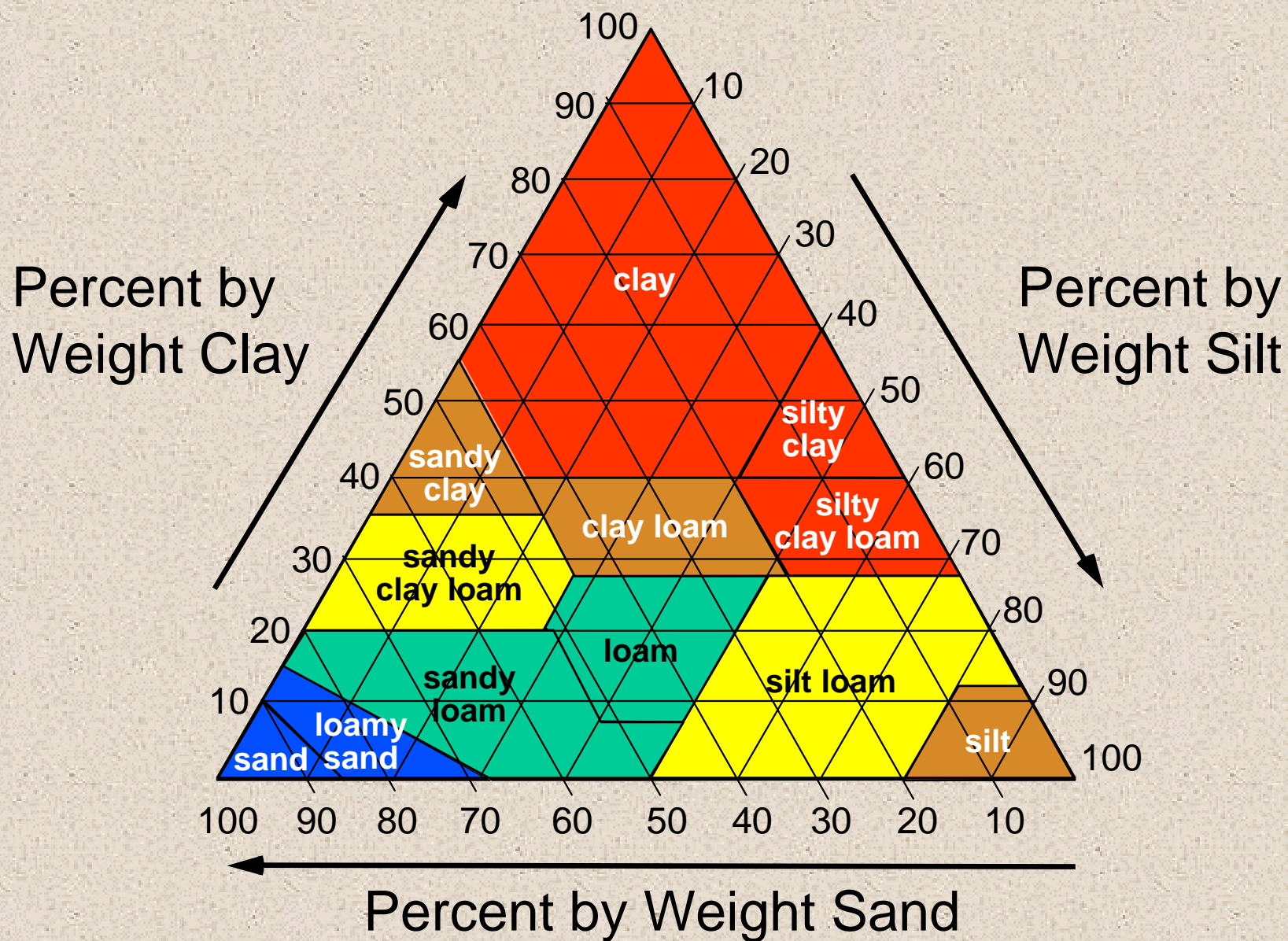
Thermal desorption system should:

- automatically leak check each tube
- include a tube conditioning system
- automatically add internal standards



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Sub-Slab Air Permeability Testing

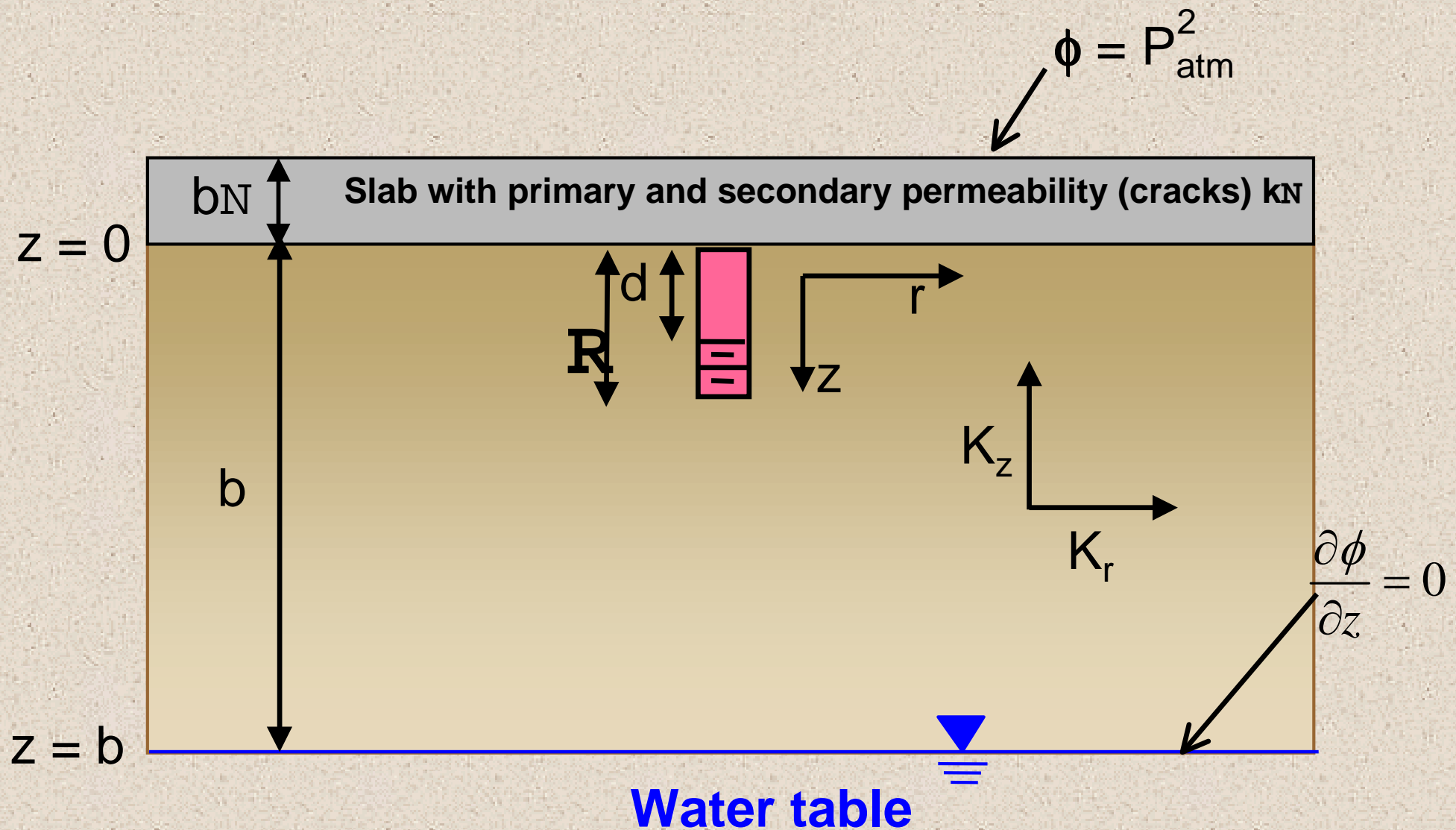


USDA Soil Textural Diagram

Gas Permeability of USDA Textures

Texture	k_i (cm ²)	- 0.33 bar		- 15 bar	
		k_r	k_a (cm ²)	k_r	k_a (cm ²)
Sand	6.07E-08	0.66	4.00E-08	0.89	5.40E-08
Loamy sand	1.77E-08	0.55	9.74E-09	0.82	1.45E-08
Sandy loam	7.55E-09	0.32	2.42E-09	0.68	5.13E-09
Loam	3.81E-09	0.18	6.86E-10	0.59	2.24E-09
Silt loam	1.96E-09	0.12	2.35E-10	0.56	1.10E-09
Sandy clay loam	1.24E-09	0.15	1.86E-10	0.45	5.58E-10
Clay loam	6.71E-10	0.12	8.05E-11	0.42	2.82E-10
Silty clay loam	4.38E-10	0.05	2.19E-11	0.34	1.49E-10
Sandy clay	3.47E-10	0.05	1.74E-11	0.25	8.67E-11
Silty clay	2.60E-10	0.04	1.04E-11	0.26	6.76E-11
Clay	1.73E-10	0.03	5.19E-12	0.22	3.81E-11

Conceptual Model for Gas Permeability Testing



Governing Equation and Boundary Conditions for Steady-State Testing (Baehr and Joss, 1995)

$$k_r \left(\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} \right) + k_z \frac{\partial^2 \phi}{\partial z^2} = 0$$

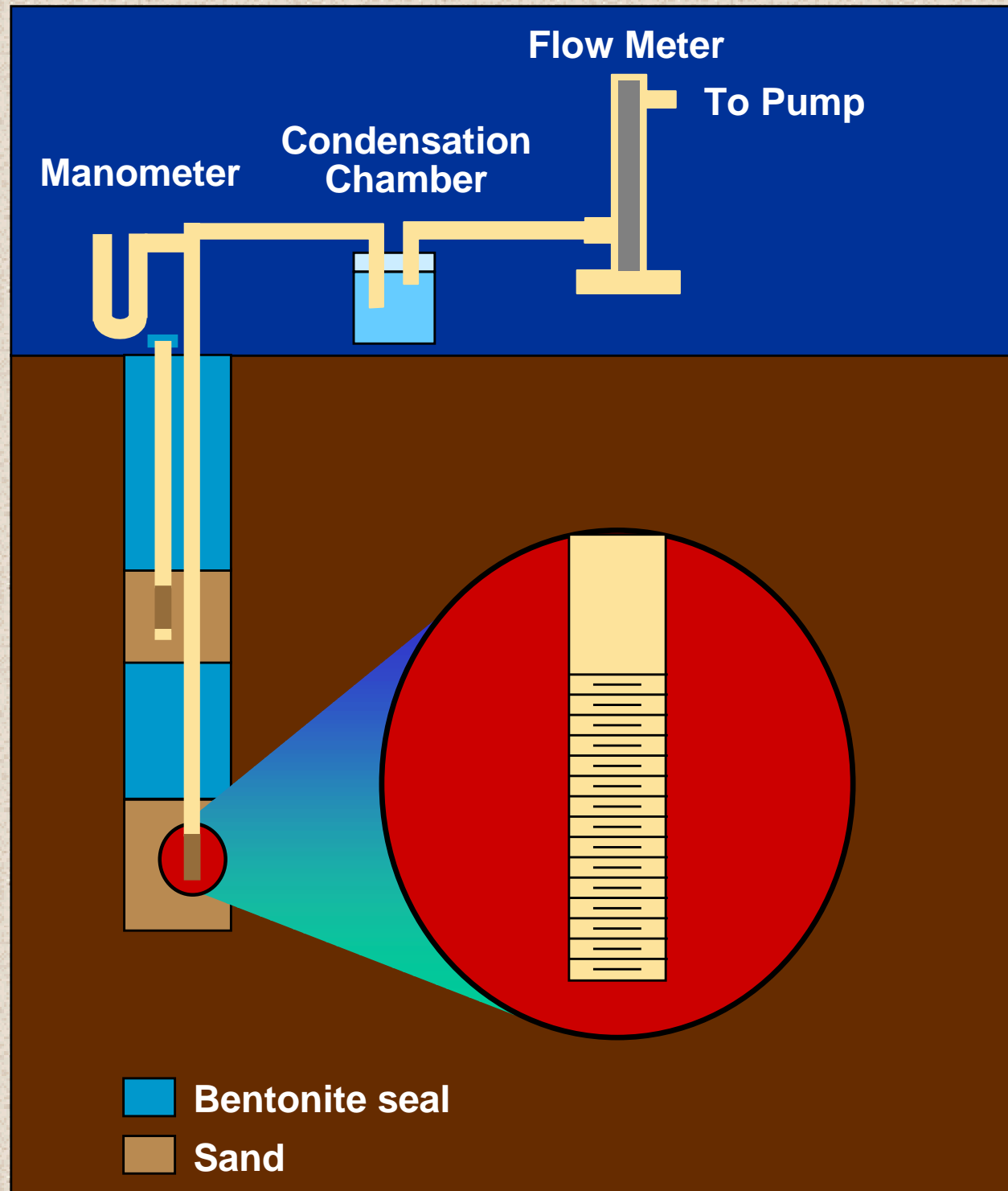
$$k_z \left. \frac{\partial \phi}{\partial z} \right|_{z=0} = \frac{k'}{b'} (\phi - \phi_{atm})$$

$$\lim_{r \rightarrow \infty} \phi = \phi_{atm}$$

$$k_z \left. \frac{\partial \phi}{\partial z} \right|_{z=b} = 0$$

$$k_r \left. \frac{\partial \phi}{\partial r} \right|_{r=r_w} = - \frac{Q_m \mu_g \mathcal{R} T}{\pi M_g (d_L - d_U) r_w}$$

Schematic for Steady-State, Single-Interval Testing



Correction for Frictional Head Loss (Joss and Baehr, 1997)

$$f = \frac{d}{L} \left(\frac{1}{\bar{\phi}} - \frac{1}{C} \right) (\phi_1 - \phi_{atm})$$

$$C = \left(v \rho_g \right)^2 \frac{\Re T}{M_g}$$

$$\phi = \phi_1 \pm \frac{L}{d} \left[\frac{C |f|}{C \left(1/\bar{\phi} \right) - 1} \right]$$

$$\bar{\phi} = \frac{\phi_1 + \phi_{atm}}{2}$$

Equipment for Single-Interval Testing



Example Output

Results of gas permeability testing at MWE-02-02

Test	Q _m (g/s)) P (in water)	Estimated P _{well} (atm)	Lower Estimate of k _r (cm ²)	Upper Estimate of k _r (cm ²)
1e	-0.373	-125.20	0.69215	1.14 x 10 ⁻⁹	3.21 x 10 ⁻⁹
2e	-0.438	-148.00	0.63609	1.17 x 10 ⁻⁹	3.30 x 10 ⁻⁹
3e	-0.453	-164.56	0.59537	1.11 x 10 ⁻⁹	3.14 x 10 ⁻⁹
			mean	1.14 x 10 ⁻⁹	3.22 x 10 ⁻⁹
			95% CI*	1.07 x 10 ⁻⁹ - 1.21 x 10 ⁻⁹	3.02 x 10 ⁻⁹ - 3.42 x 10 ⁻⁹
1i	0.363	62.07	1.15262	1.75 x 10 ⁻⁹	4.96 x 10 ⁻⁹
2i	0.533	92.15	1.22658	1.68 x 10 ⁻⁹	4.74 x 10 ⁻⁹
3i	0.815	126.70	1.31154	1.79 x 10 ⁻⁹	5.08 x 10 ⁻⁹
			mean	1.74 x 10 ⁻⁹	4.93 x 10 ⁻⁹
			95% CI*	1.60 x 10 ⁻⁹ - 1.88 x 10 ⁻⁹	4.50 x 10 ⁻⁹ - 5.36 x 10 ⁻⁹

* t-distribution

**Simulated Pressure
Differential (Pa)
Below a Slab During
Steady-State,
Multiple-Interval Air
Permeability Testing**

Flow = 5.6 g/s (10 scfm)

$L_{\text{slab}} = 13 \text{ cm}$

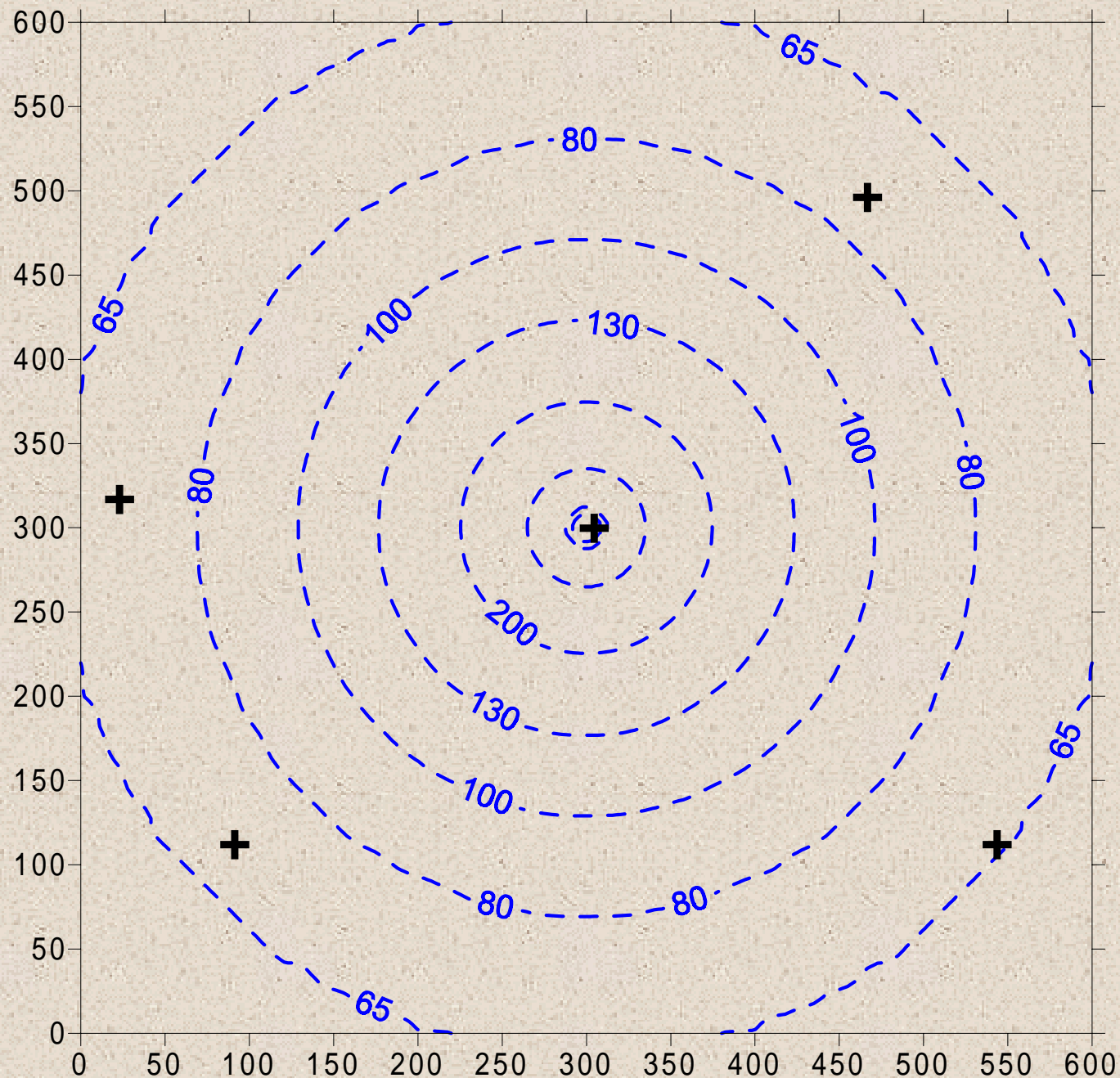
$L_{\text{water-table}} = 1000 \text{ cm}$

$K_{\text{slab}} = 1.0 \times 10^{-10} \text{ cm}^2$

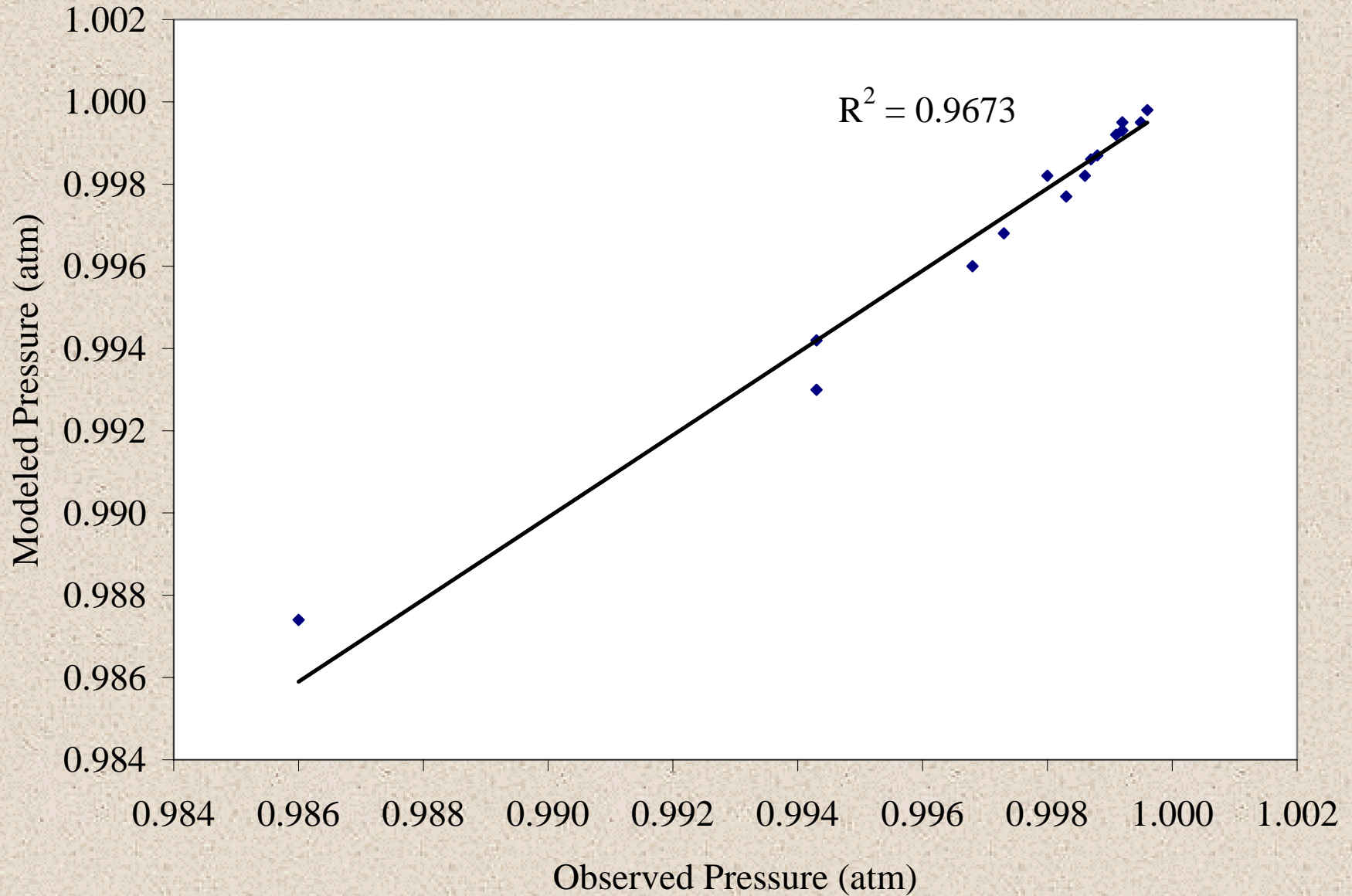
$K_{\text{soil}} = 1.0 \times 10^{-06} \text{ cm}^2$

$R_w = 1.3 \text{ cm}$

$\alpha_g = 0.2$



QA: Simulated Versus Observed Pressure for Steady-State, Multiple Interval Air Permeability Testing



Questions?



How could vapors migrate to this house?